
UNIVERSITI SAINS MALAYSIA

First Semester Examination
2009/2010 Academic Session

November 2009

KOT 222 – Organic Chemistry II
[Kimia Organik II]

Duration : 3 hours
[Masa : 3 jam]

Please check that this examination paper consists of TWENTY FOUR pages of printed material before you begin the examination.

Instructions:

Answer any **FIVE** (5) questions.

You may answer the questions either in Bahasa Malaysia or in English.

If a candidate answers more than five questions, only the answers to the first five questions in the answer sheet will be graded.

In the event of any discrepancies, the English version shall be used.

...2/-

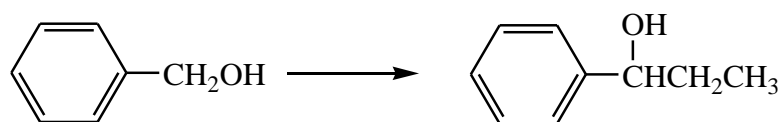
1. (a) Show how would you prepare 1-butanol from:

- (i) an alkene
- (ii) 1-bromobutane
- (iii) 1-bromopropane
- (iv) bromoethane
- (v) 3-butenal

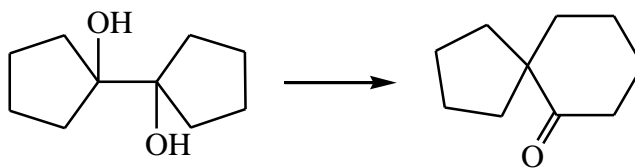
(10 marks)

(b) Show the synthetic steps which could be used for the following transformations:

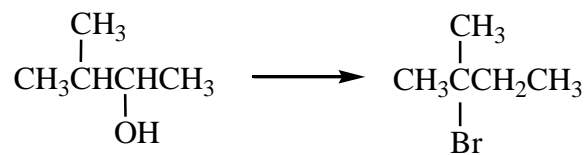
(i)



(ii)

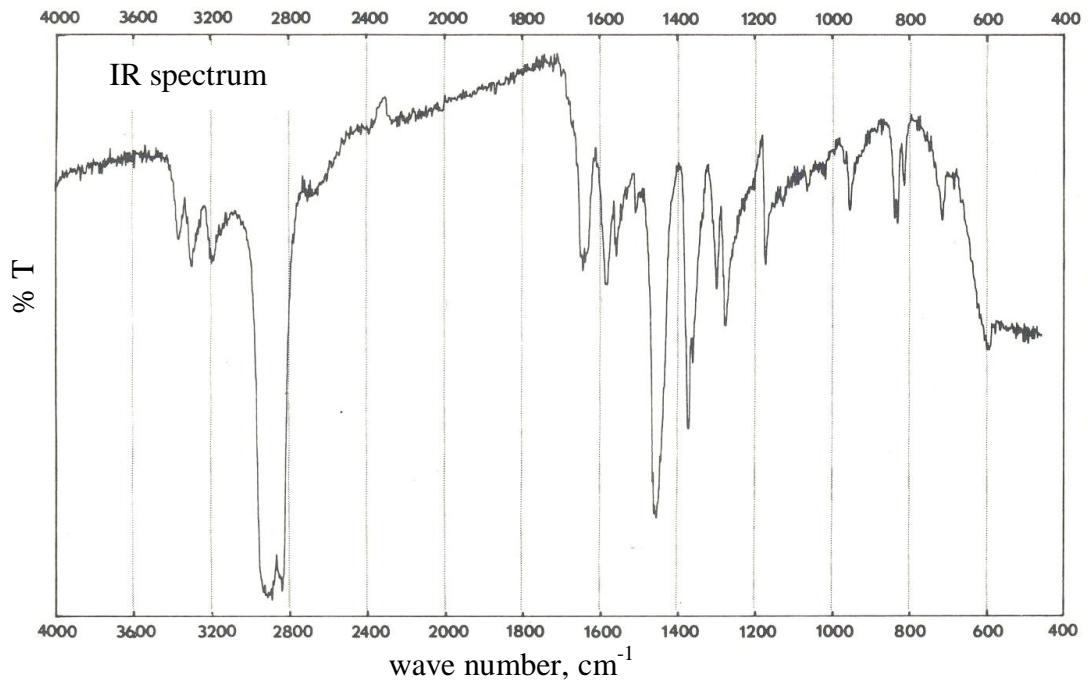
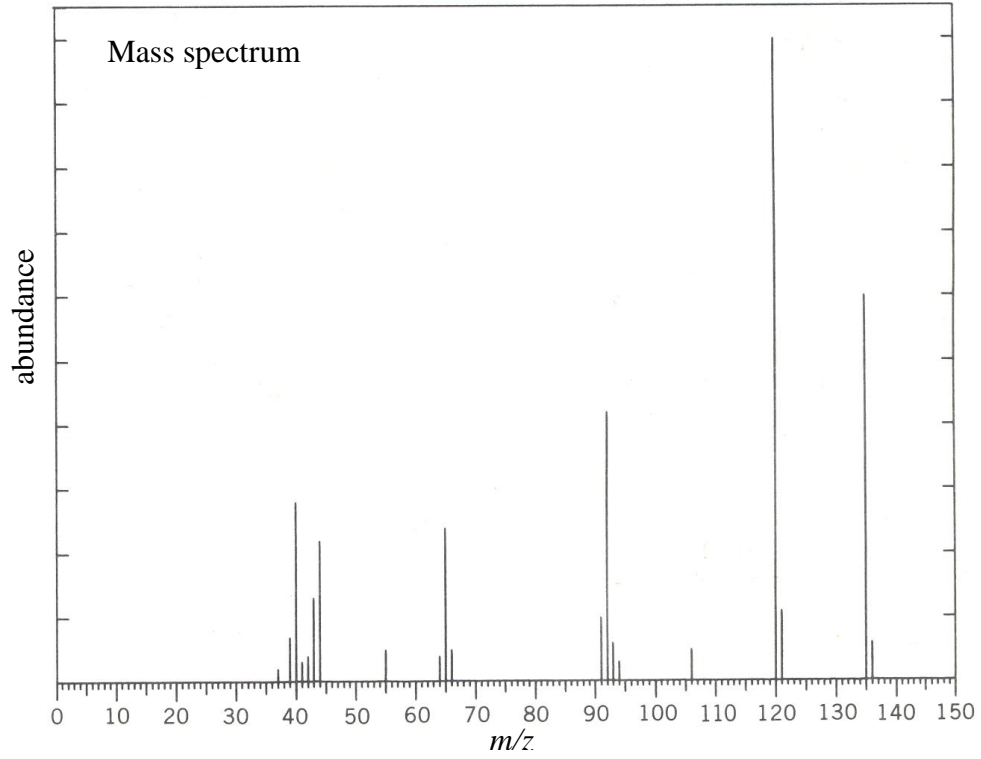


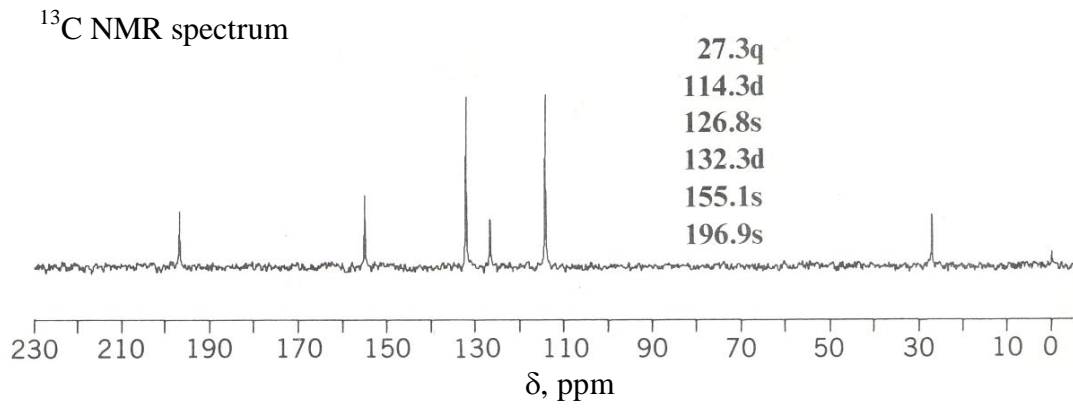
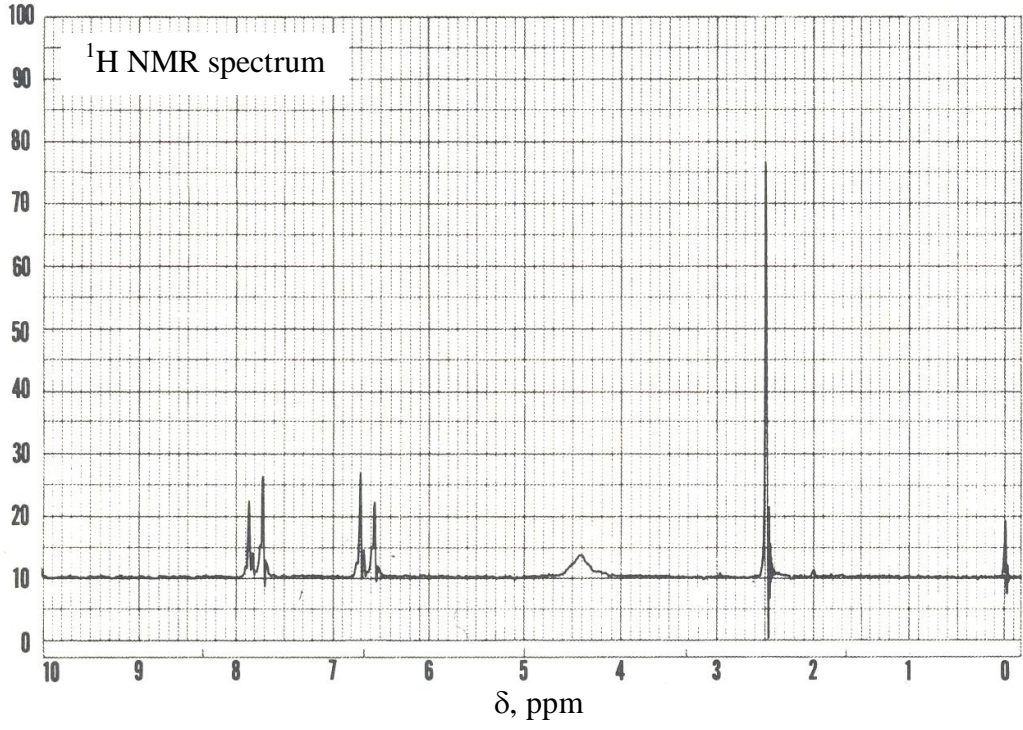
(iii)



(10 marks)

2. The IR, ^1H NMR, ^{13}C NMR and mass spectra of compound **A** having a molecular weight of 135.0685 are given below. Deduce the structure of compound **A**. The base peak is found at m/z 120. Draw the structure of the fragment ion that gives rise to this peak and explain why it is particularly stable.



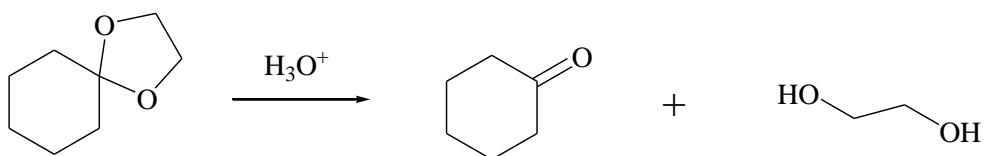


(20 marks)

3. (a) Give structures for compounds **A** through **I** in the conversions below:

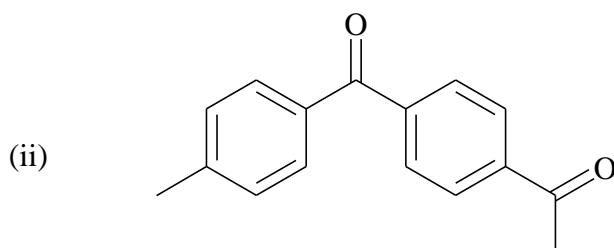
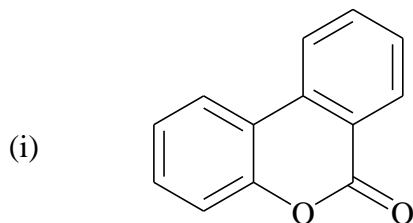
(14 marks)

- (b) Propose a mechanism for the following reaction:



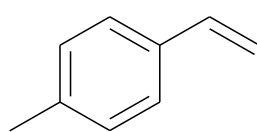
(6 marks)

4. (a) Predict the major products of bromination of the following compounds, using Br_2 and FeBr_3 in the dark:

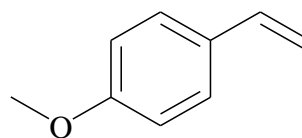


(6 marks)

- (b) Which of the following compounds reacts with HBr more rapidly? Explain.

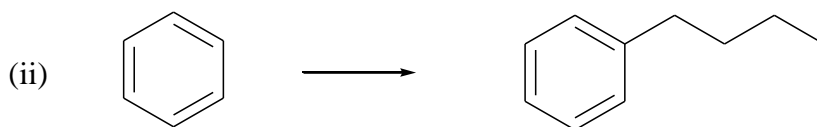
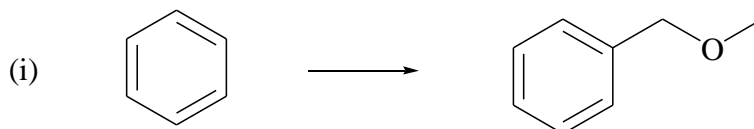


or



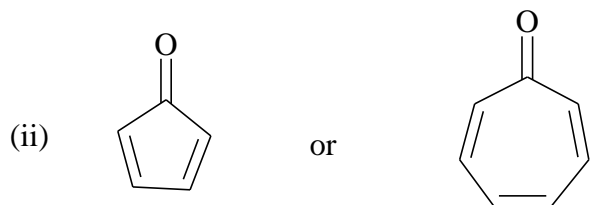
(4 marks)

- (c) Show how the following compounds can be synthesized from the starting materials indicated.



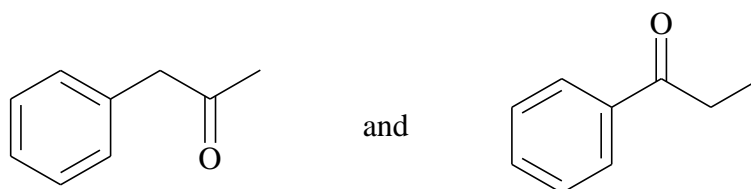
(10 marks)

5. (a) Which ion/compound in each of the following pairs is more stable? Explain, using the polygon rule.



(5 marks)

- (b) Identify the IR absorption band that could be used to distinguish the following pair of compounds.



(3 marks)

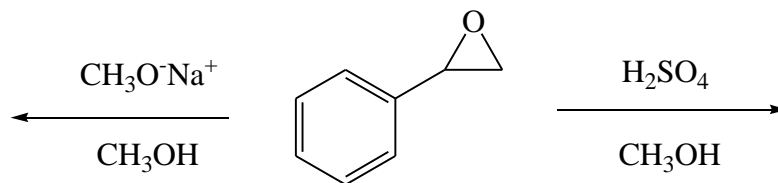
- (c) Sketch the ^1H NMR spectrum of each of the compounds in Question 5 (b), showing the approximate chemical shifts and multiplicity for each of the proton signals.

(6 marks)

- (d) Suggest the synthesis of each of the compounds in Question 5 (b), utilizing either benzene or toluene as the starting material.

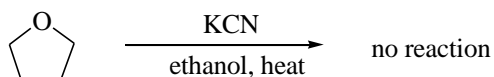
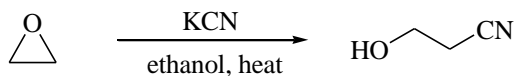
(6 marks)

6. (a) Give the product and mechanism of each reaction shown below. Explain why nucleophilic attack on the epoxide occurs at different sites in the two reactions.



(4 marks)

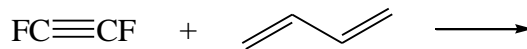
- (b) Explain why ethylene oxide is attacked by cyanide ion but tetrahydrofuran is not.



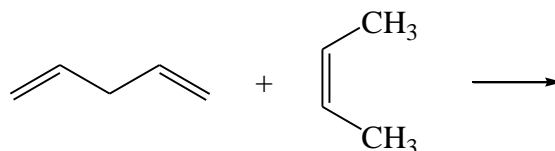
(2 marks)

- (c) Provide product for each of the following reactions. Explain your reasoning.

(i)



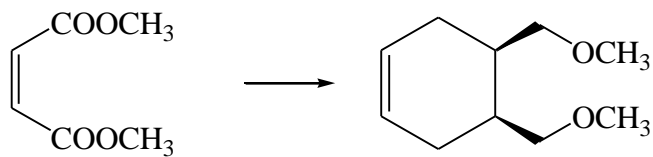
(ii)



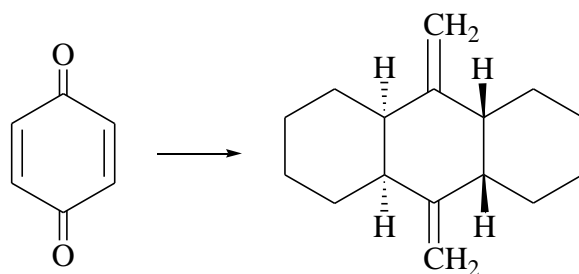
(4 marks)

(d) Suggest reactions to carry out each transformation. Each case requires more than one step.

(i)

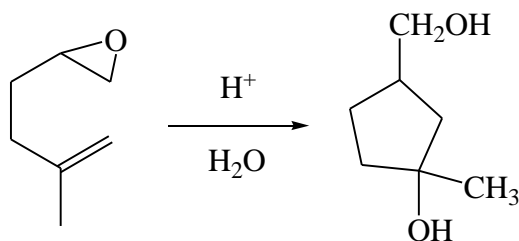


(ii)



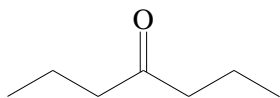
(7 marks)

(e) The following reaction resembles the acid-catalyzed cyclization of squalene oxide. Propose a mechanism for this reaction.

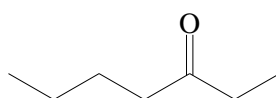


(3 marks)

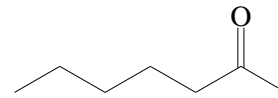
7. (a) Identify significant fragment ion peaks and hence assign the spectra **1**, **2** and **3** below to the following isomeric ketones **A**, **B** and **C**. Explain your reasoning.



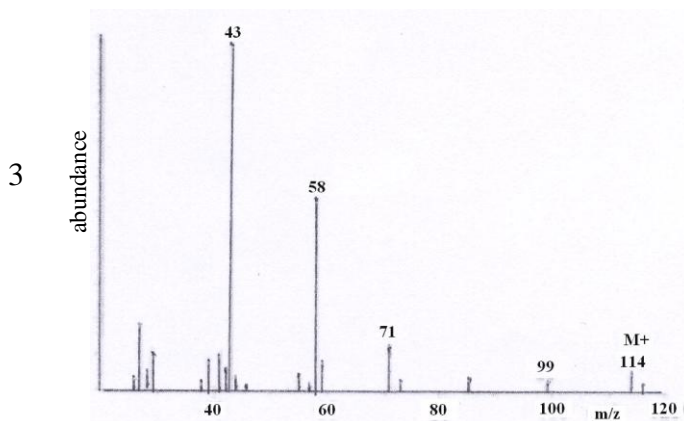
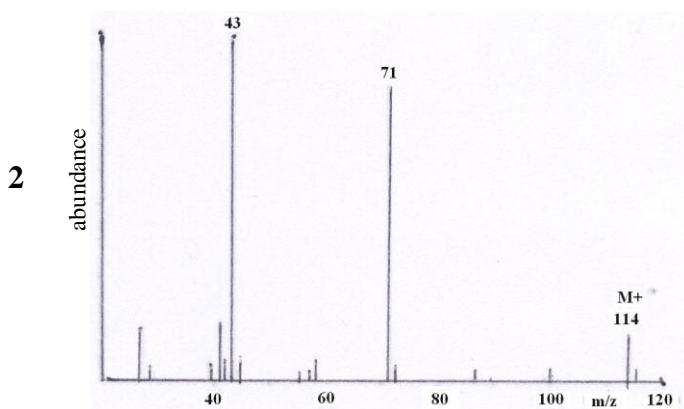
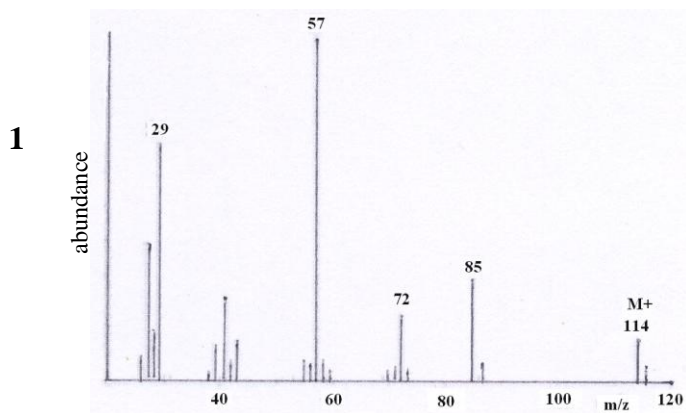
A



B

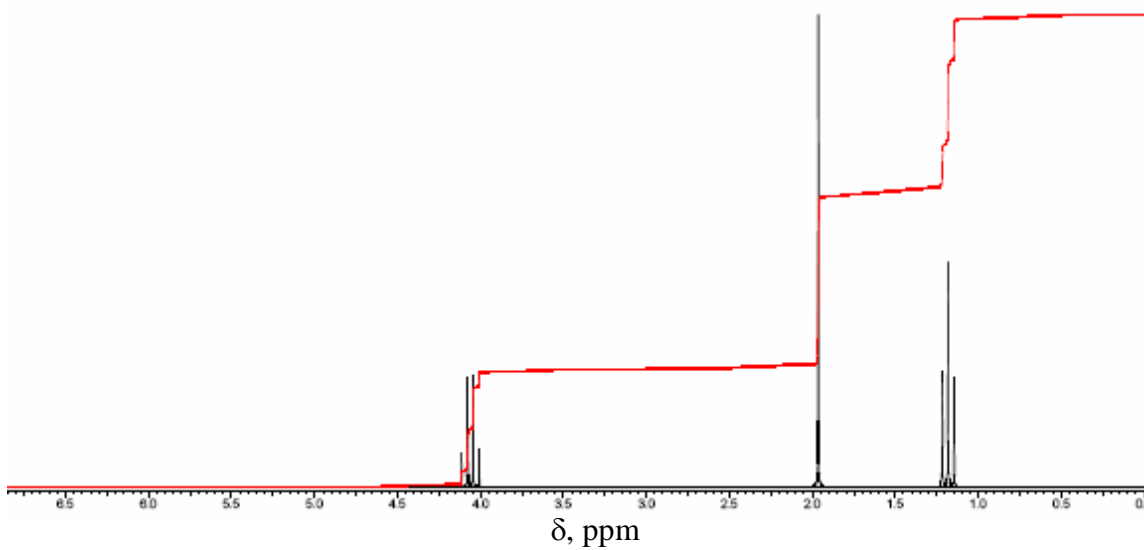
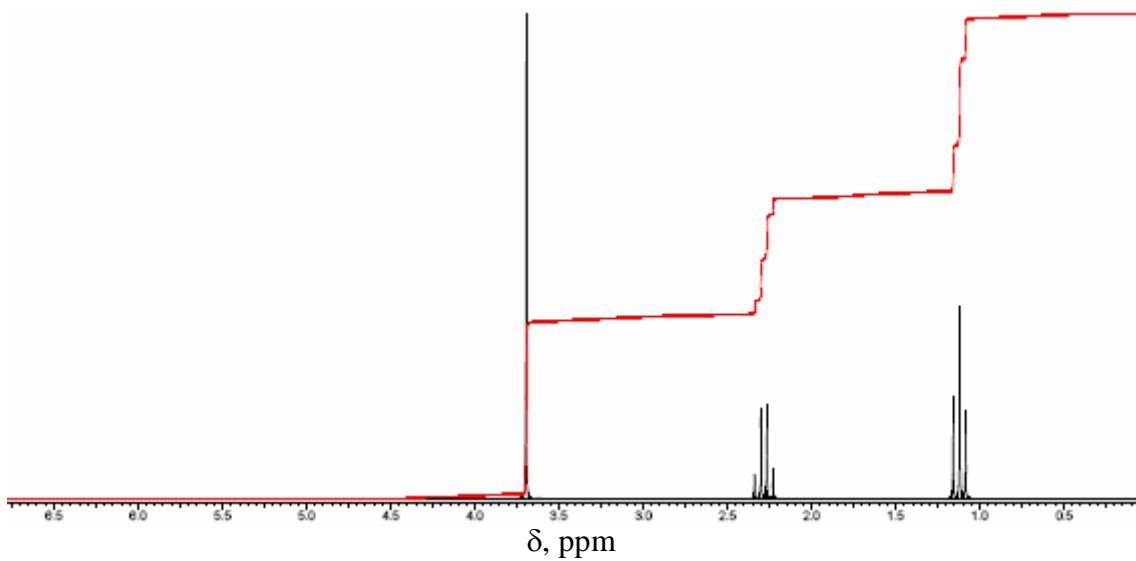
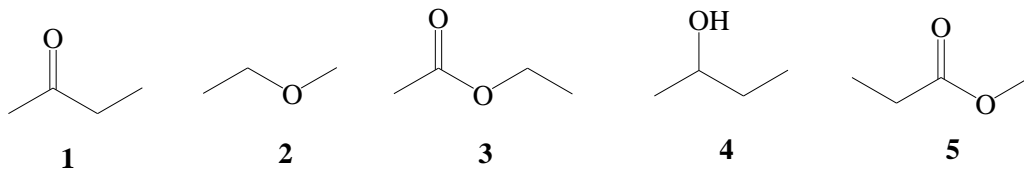


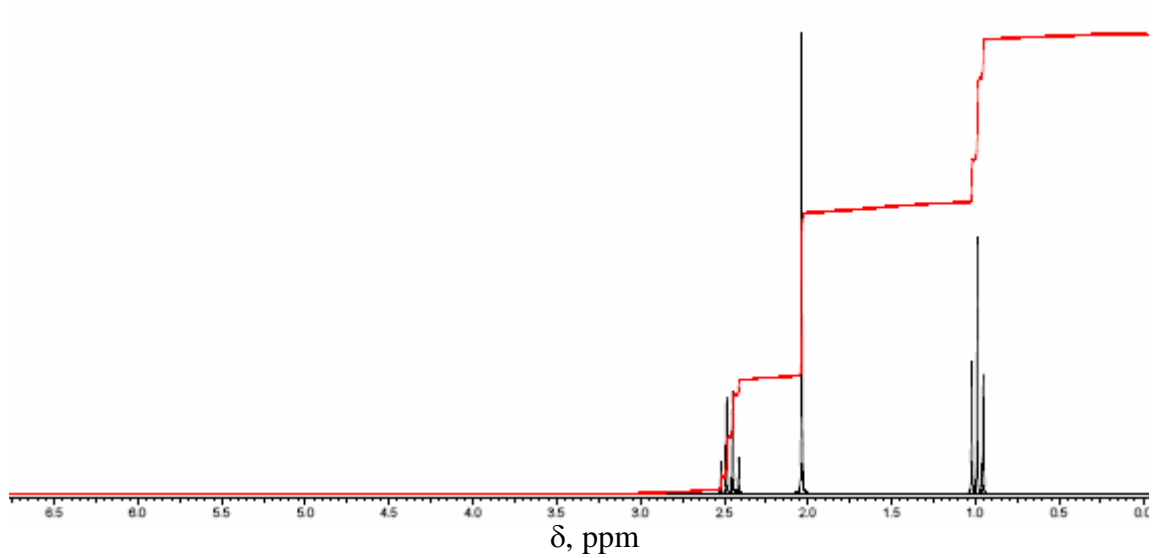
C



(9 marks)

- (b) (i) Match **three** of the following compounds **1-5** to the three ^1H NMR spectra **A, B** and **C**. Give reasons for your choice.





(8 marks)

- (ii) Explain how IR spectra can be used to distinguish compounds **1**, **2** and **4** in Question 7 (b) (i).

(3 marks)

TERJEMAHAN

Arahan:

Jawab **LIMA** (5) soalan.

Anda dibenarkan menjawab soalan ini sama ada dalam Bahasa Malaysia atau Bahasa Inggeris.

Jika calon menjawab lebih daripada lima soalan, hanya lima soalan pertama mengikut susunan dalam skrip jawapan akan diberi markah.

Sekiranya terdapat sebarang percanggahan pada soalan peperiksaan, versi Bahasa Inggeris hendaklah diguna pakai.

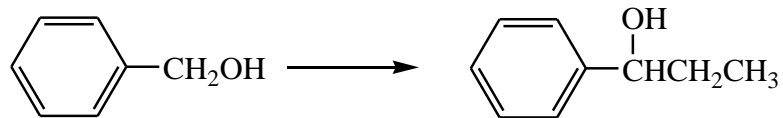
1. (a) Tunjukkan bagaimana anda menyediakan 1-butanol daripada:

- (i) suatu alkena
- (ii) 1-bromobutana
- (iii) 1-bromopropana
- (iv) 1-bromoetana
- (v) 3-butenal

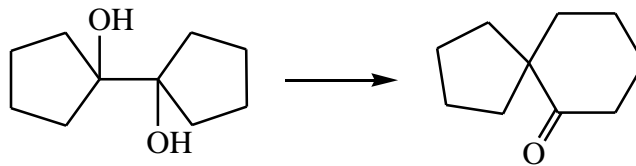
(10 markah)

(b) Tunjukkan langkah sintetik yang boleh digunakan bagi transformasi berikut:

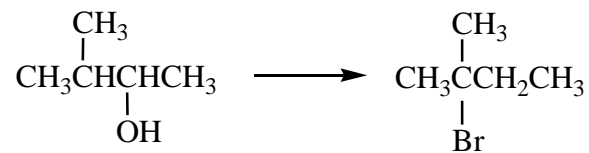
(i)



(ii)

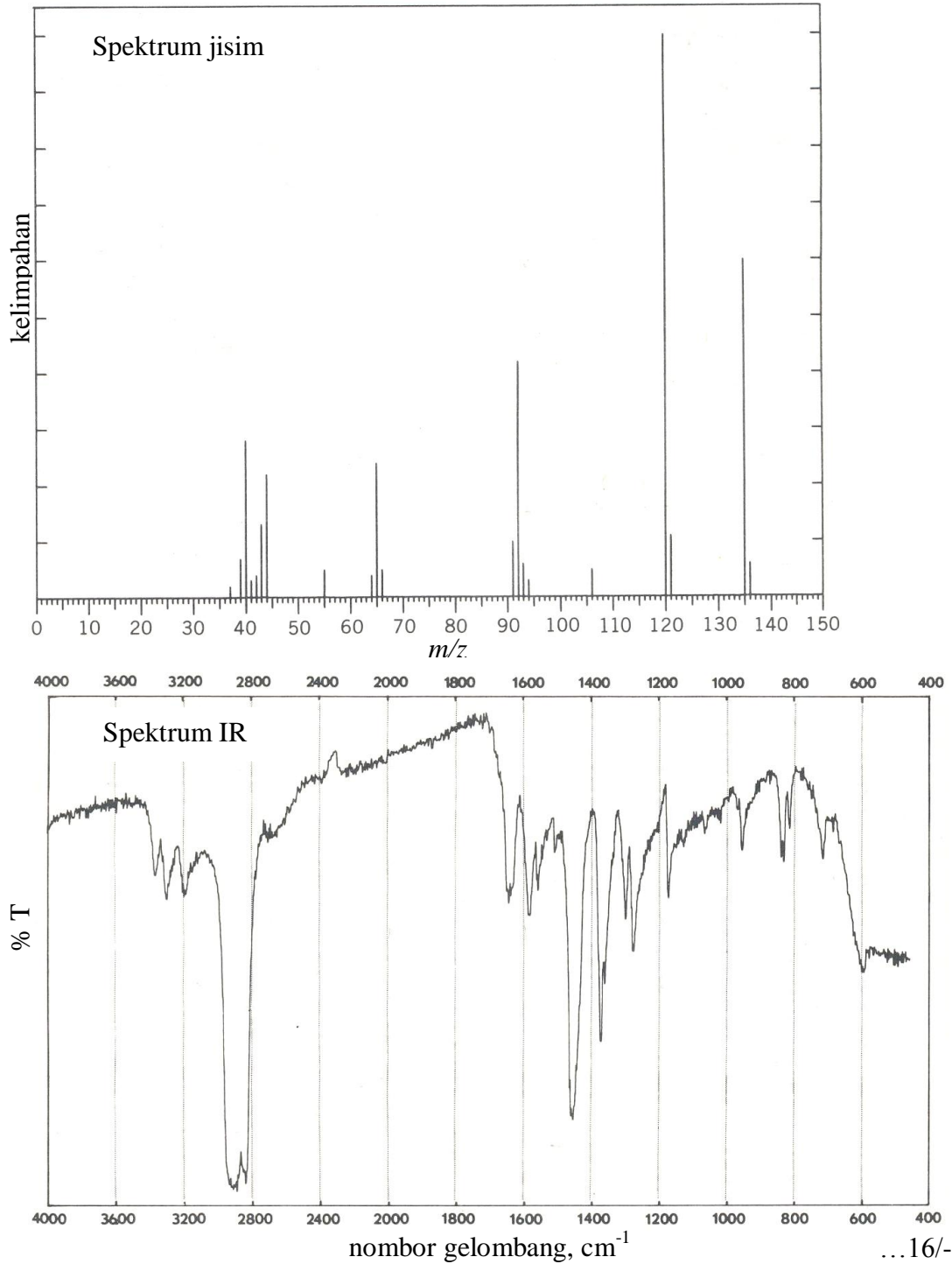


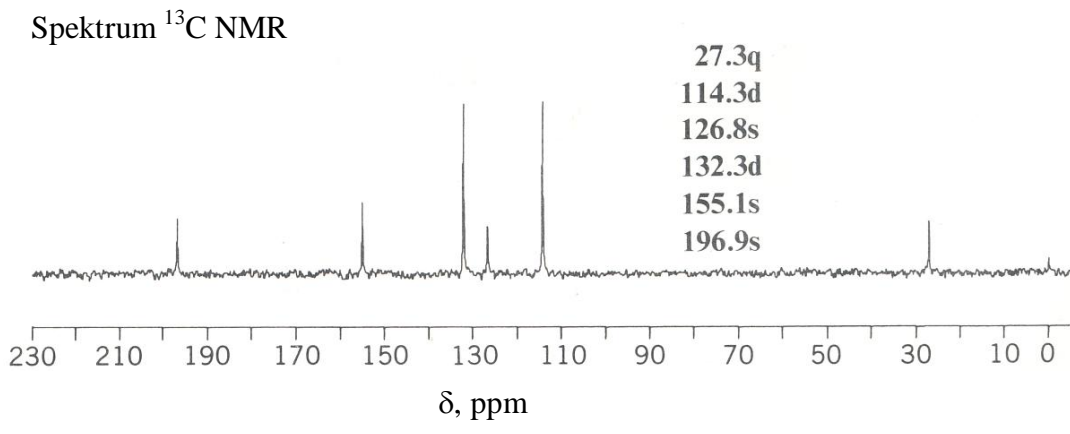
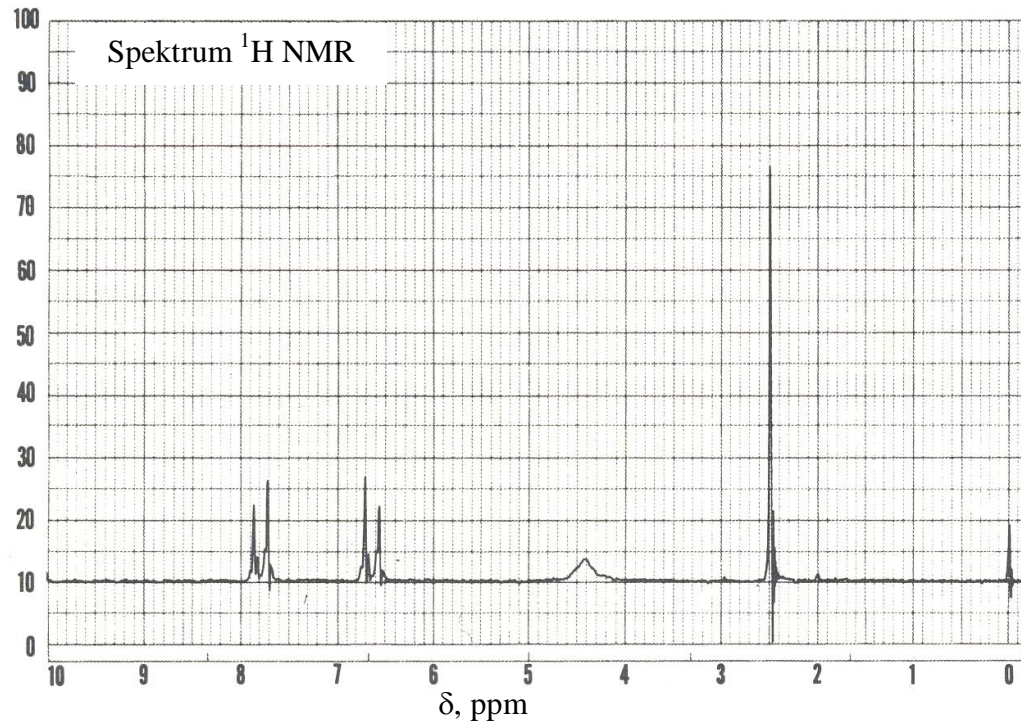
(iii)



(10 markah)

2. Spektrum IR, ^1H NMR, ^{13}C NMR and jisim untuk suatu sebatian **A** dengan berat molekul 135.0685 telah diberi di bawah. Terangkan penentuan struktur sebatian **A**. Puncak asas didapati pada m/z 120. Lukiskan struktur ion fragmen bagi puncak ini dan terangkan kestabilannya.



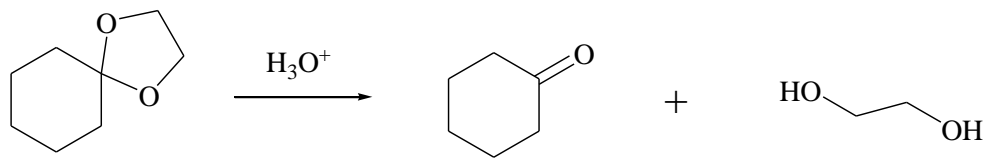


(20 markah)

3. (a) Berikan struktur bagi sebatian **A** hingga **I** dalam penukaran di bawah:

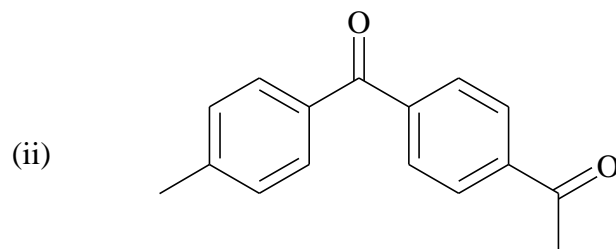
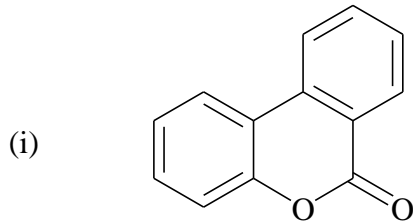
(14 markah)

- (b) Cadangkan suatu mekanisme bagi tindak balas berikut:



(6 markah)

4. (a) Ramalkan hasil utama pembrominan setiap sebatian berikut dengan menggunakan Br_2 dan FeBr_3 dalam keadaan gelap:



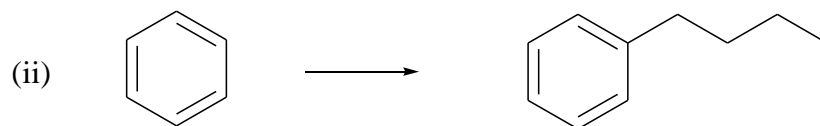
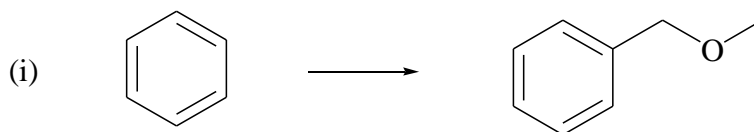
(6 markah)

- (b) Sebatian manakah akan bertindak balas dengan HBr pada kadar lebih cepat? Jelaskan.



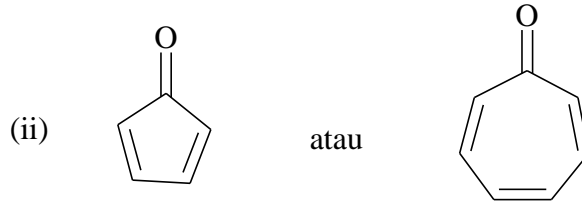
(4 markah)

- (c) Tunjukkan bagaimana setiap sebatian berikut dapat disintesis daripada bahan permulaan yang ditunjukkan.



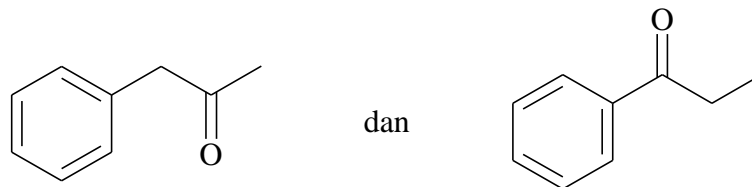
(10 markah)

5. (a) Dalam setiap pasangan berikut, ion/sebatian manakah yang lebih stabil? Jelaskan dengan menggunakan peraturan poligon.



(5 markah)

- (b) Kenalpastikan jalur penyerapan IR yang dapat digunakan untuk membezakan pasangan sebatian yang berikut:



(3 markah)

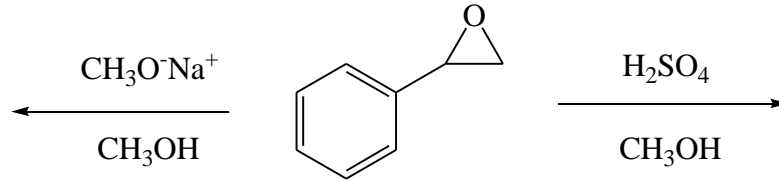
- (c) Lakarkan spektrum ^1H NMR bagi setiap sebatian dalam Soalan 5 (b). Tunjukkan anjakan kimia dan pengkupelan yang dijangkakan bagi setiap isyarat proton.

(6 markah)

- (d) Cadangkan sintesis bagi setiap sebatian dalam Soalan 5 (b) dengan menggunakan benzena atau toluena sebagai bahan permulaan.

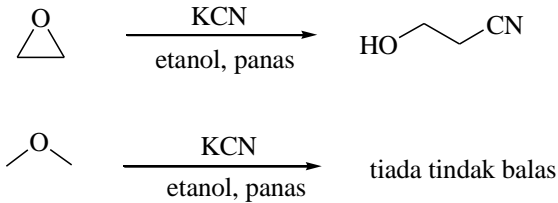
(6 markah)

6. (a) Berikan hasil dan mekanisme setiap tindak balas yang ditunjukkan di bawah. Terangkan mengapa serangan nukleofil ke atas epoksida berlaku pada tempat yang berbeza dalam dua tindak balas ini.



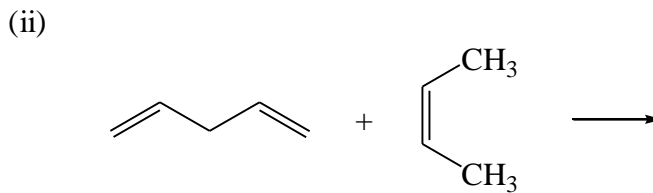
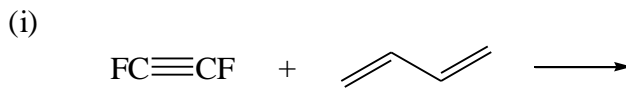
(4 markah)

- (b) Terangkan mengapa ion sianida menyerang etilena oksida dan bukannya tetrahidrofuran.



(2 markah)

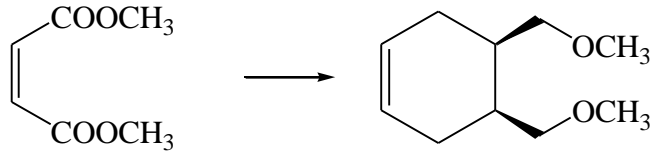
- (c) Berikan hasil bagi setiap tindak balas berikut. Terangkan alasan anda.



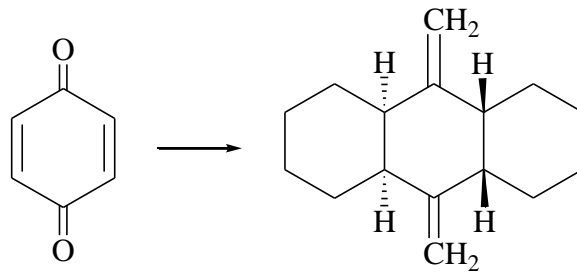
(4 markah)

(d) Cadangkan tindak balas bagi setiap transformasi. Setiap kes memerlukan lebih daripada satu langkah.

(i)

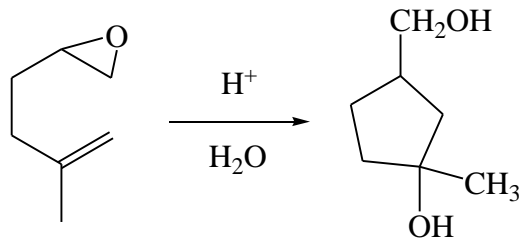


(ii)



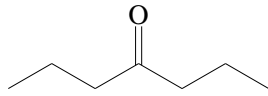
(7 markah)

(e) Tindak balas berikut ialah pensiklikan bermangkin asid bagi skualena oksida. Cadangkan mekanisme untuk tindak balas ini.

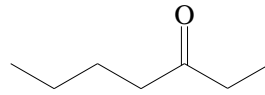


(3 markah)

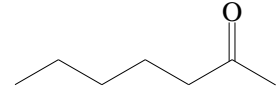
7. (a) Kenalpastikan fragmen bagi puncak ion yang penting dan seterusnya padankan spektrum 1, 2 dan 3 di bawah dengan isomer keton A, B dan C. Terangkan alasan anda.



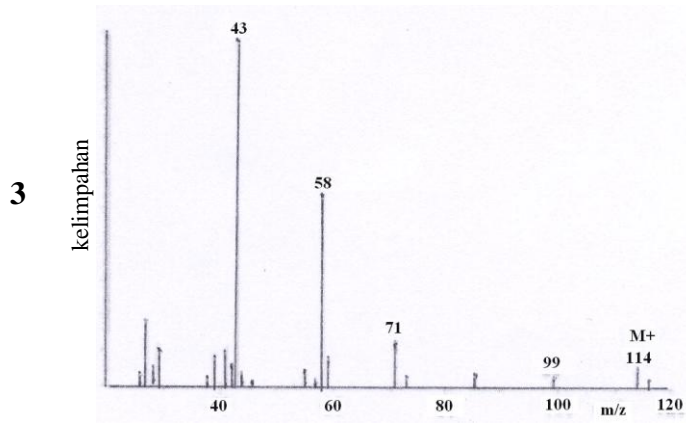
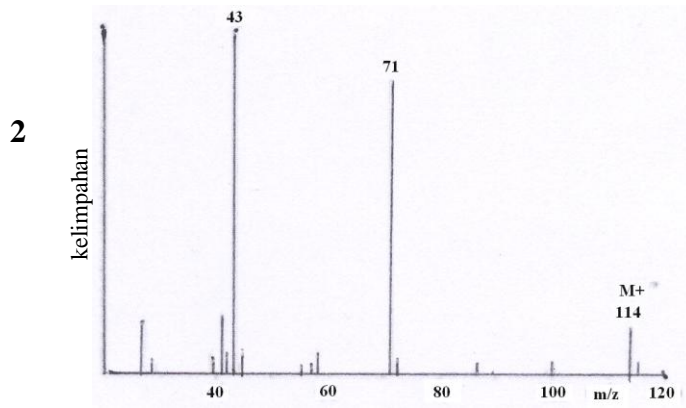
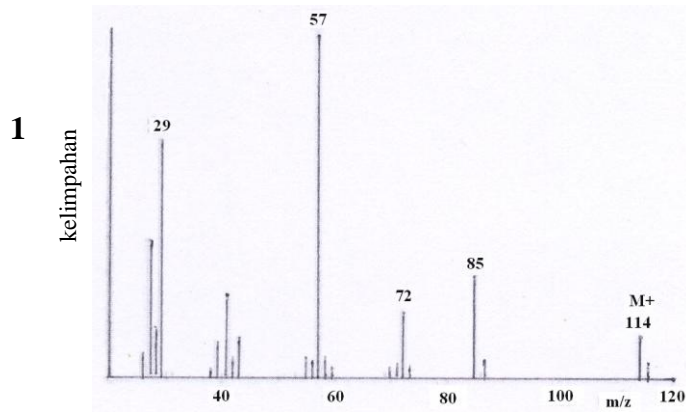
A



B

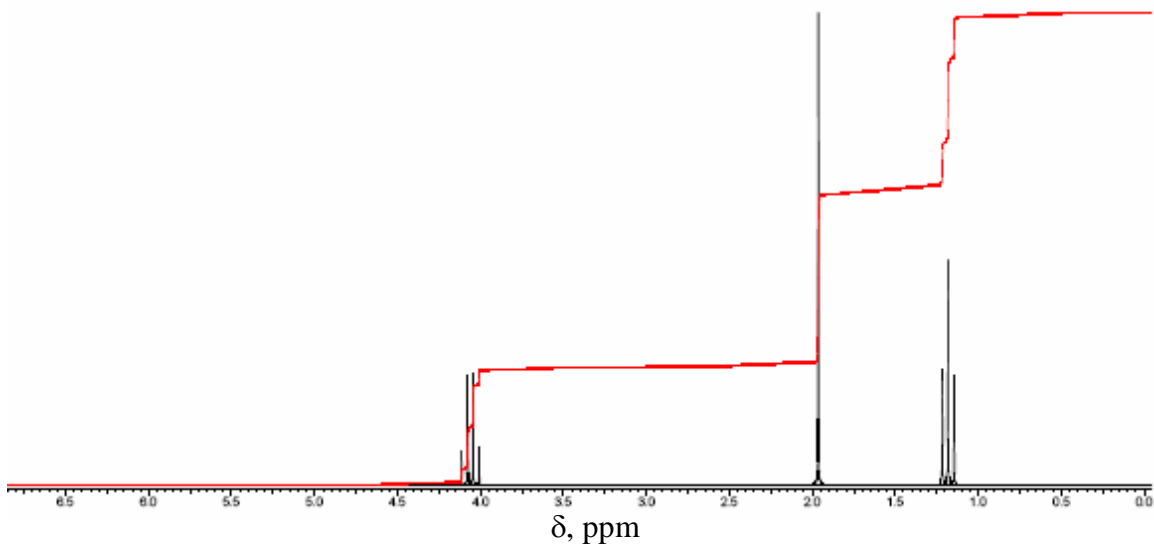
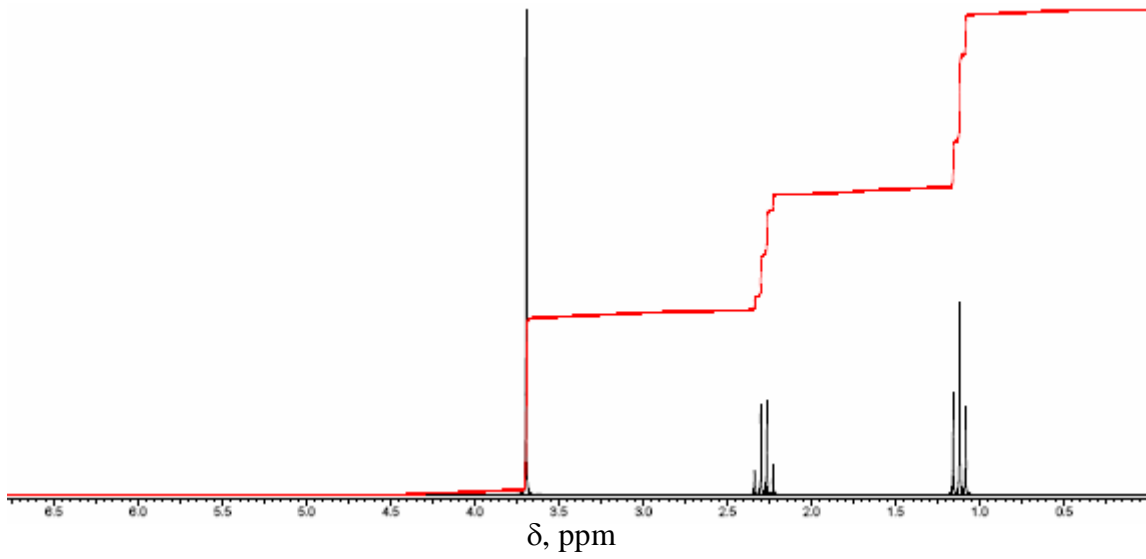
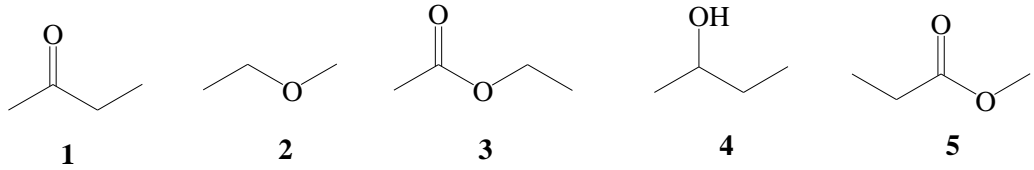


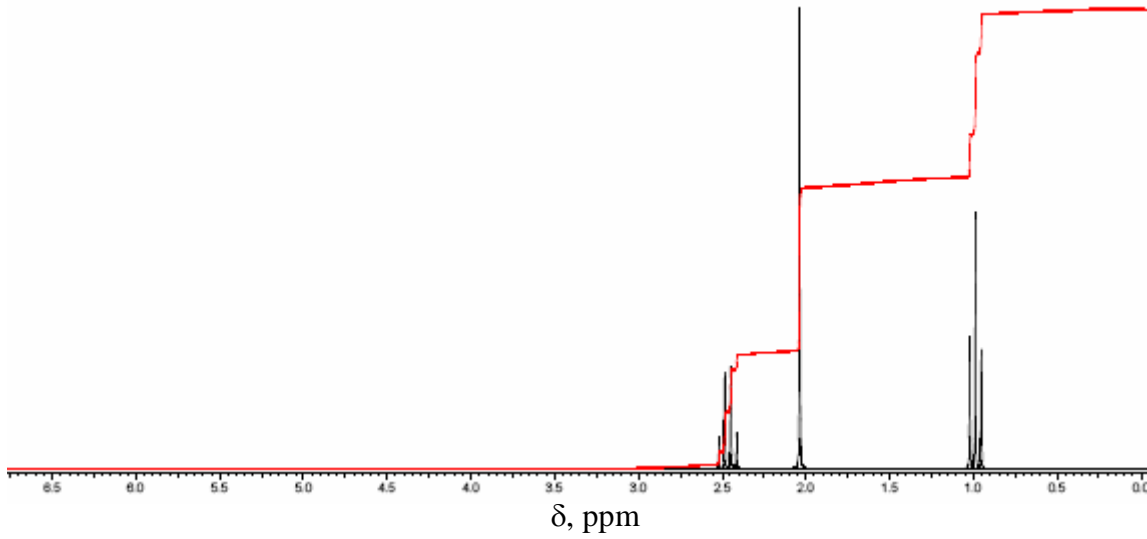
C



(9 markah)
...23/-

- (b) (i) Padankan **tiga** daripada sebatian **1-5** berikut dengan tiga spektrum ^1H NMR, **A**, **B** dan **C**. Berikan alasan bagi pilihan anda.





(8 markah)

- (ii) Terangkan bagaimana spektrum IR boleh digunakan untuk menentukan sebatian **1**, **2** and **4** dalam Soalan 7 (b) (i).

(3 markah)